Renewable and Sustainable Energy Reviews 31 (2014) 531–542

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

A review of microencapsulation methods of phase change materials (PCMs) as a thermal energy storage (TES) medium

A. Jamekhorshid [a], S.M. Sadrameli [a,*], M. Farid [b]

[a] Faculty of Chemical Engineering, Tarbiat Modares University, Tehran, Iran
[b] Department of Chemical and Material Engineering, The University of Auckland, Auckland, New Zealand

ARTICLE INFO

Article history:
Received 5 February 2013
Received in revised form
9 December 2013
Accepted 19 December 2013
Available online 20 January 2014

Keywords:
Thermal energy storage
Phase change material
PCM
Microencapsulation method
Microcapsule

ABSTRACT

Microencapsulation of phase change materials (PCMs) is an effective way of enhancing their thermal conductivity and preventing possible interaction with the surrounding and leakage during the melting process, where there is no complete overview of the several methods and techniques for microencapsulation of different kinds of PCMs that leads to microcapsules with different morphology, structure, and thermal properties. In this paper, microencapsulation methods are perused and classified into three categories, i.e. physical, physic-chemical, and chemical methods. It summarizes the techniques used for microencapsulation of PCMs and hence provides a useful tool for the researchers working in this area. Among all the microencapsulation methods, the most common methods described in the literature for the production of microencapsulated phase change materials (MEPCMs) are interfacial polymerization, suspension polymerization, coacervation, emulsion polymerization, and spray drying.

Contents

1. Introduction

Phase change materials (PCMs) are substances which melts and solidifies at a nearly constant temperature, and are capable of

* Corresponding author.: Tel./fax: +98 21 82884902.
E-mail address: sadramel@modares.ac.ir (S.M. Sadrameli).

1364-0321/$ - see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.rser.2013.12.033

storing and releasing large amounts of energy when undergoes phase change. They are developed for various applications such as thermal comfort in building, thermal protection, cooling, air-conditioning, and for solar heating systems. Comprehensive reviews on PCM types and their applications are given by Farid et al. [1], Khudhair et al. [2], Zalba et al. [3], and Sharma et al. [4].

Employing PCMs in traditional manner has several defects, such as the necessity of using special latent heat devices or heat exchange surface which increase the associated cost and thermal resistant between the PCM and the environment [5]. Comprehensive investigations have been done on new type PCM called form-stable or shape-stabilized PCM, which prepared by blending the PCM with a supporting material, usually polymers, and further treatments [5–9]. These composites would be applied directly in different applications with no extra devices or elements. Although these composites can keep their shape during the phase change from solid to liquid, the PCM tends to diffuse to surface and loose gradually [10].

In order to prevent leakage of the melted PCM during the phase change process in latent heat thermal energy storage (LHTES) systems, increase the heat transfer rate, reduce PCM reactivity with the outside environment and control the changes in the volume as phase change occurs, microencapsulation is probably the best solution [11].

Microencapsulation is a process of coating individual particles or droplets with a continuous film to produce capsules in a micrometer to millimeter in size, known as a microcapsule [12]. Microencapsulated phase change materials are composed of two main parts: a PCM as core and a polymer or inorganic shell as PCM container (Fig. 1). Microcapsules may have a regular shape (e.g. spherical, tubular, and oval) or can be made in an irregular shape. Fig. 2 illustrates the

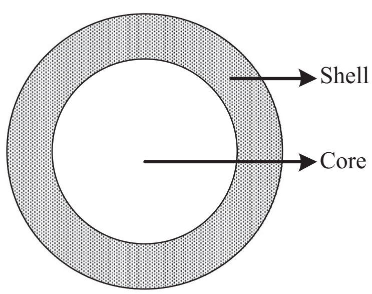


Fig. 1. Description of a microcapsule.

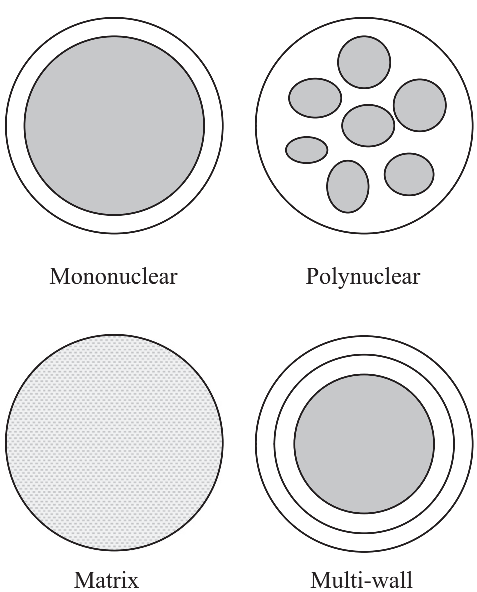


Fig. 2. Morphology of microcapsules.

typical forms of microcapsules that depend mainly on the core material and the deposition process of the shell [13].

Microencapsulated phase change materials may be used in a powder form or dispersed into a carrier fluid, e.g. water, to significantly enhance heat transfer efficiency of the carrier fluid. This kind of suspension was named as microencapsulated phase change material slurry (MPCS) [14,15]. The addition of nano-particles to MPCS was suggested by Zhang et al. [16] to improve the thermal conductivity of MPCS. However, the main limitations of the MPCS contained nano-particle are the instability and agglomeration of nano-particles and MEPCMs in carrier nano-fluid [17–19].

PCMs with a melting point ranging from -10 to 80 °C can be microencapsulated [12]. The microencapsulation technique depends on the physical and chemical properties of the materials to be used. There are several physical and chemical methods used for the production of microcapsules [12,20,21]. The most often used microencapsulation methods are as follows:

Physical methods:

i. pan coating,
ii. air-suspension coating,
iii. centrifugal extrusion,
iv. vibrational nozzle,
v. spray drying,
vi. solvent evaporation.

Physic-chemical methods:

i. Ionic gelation,
ii. coacervation,
iii. sol-gel.

Chemical methods:

i. interfacial polymerization,
ii. suspension polymerization,
iii. emulsion polymerization.

Since there are unlimited applications for microencapsulated materials such as agriculture, pharmaceuticals, foods, cosmetic and fragrances, and many other industries, most of the reviews have been focused on these applications [22–24]. There have been also few review articles and book chapters on methods of PCMs microencapsulation [21,25]. Salaün [25] briefly described coacervation, interfacial and in situ polymerization methods and review the new developments in microencapsulation process to enhance their thermal properties. Zhao and Zhang [21] reviewed interfacial, suspension, and in situ polymerization methods along with complex coacervation method. They also reviewed the applications of MEPCMs to textile and building. However, the review presented here not only covers all possible paths to microencapsulations, but also provides guidelines on the suitability of these methods to encapsulate PCM.

2. Physical methods

In these methods, the microcapsule wall is mechanically applied or condensed around the microcapsule core.

2.1. Pan coating

The pan coating process, widely used in the pharmaceutical industry, is among the oldest industrial procedures for forming small coated particles or tablets. Solid particles are mixed with a dry coating material and the temperature is raised so that the coating material melts and encloses the core particles, and then is

solidified by cooling. In an alternative method, the coating material can be gradually applied to or sprayed on the core particles tumbling in a vessel rather than being wholly mixed with the core particles from the start of encapsulation. This will save processing time and energy cost [26].

In this technique, the core melting temperature must be higher than the shell melting temperature; consequently the method cannot be used for PCM encapsulation.

2.2. Air-suspension coating

Microencapsulation by air suspension is a technique that gives improved control and flexibility compared to pan coating, via changing the times the core particles pass through the coating zone [27]. In this process, the solid particles are coated and dried while suspended in an upward moving air stream. Solutions and suspensions of coating materials in both water and volatile organic solvents are employed. However, this technique was developed for pharmaceutical industry [28], food industry [29], and cosmetic products [30] and is not suitable for encapsulating PCMs.

2.3. Centrifugal extrusion

In the centrifugal extrusion process, developed by Southwest Research Institute (SwRI) [27], the core material in its liquid phase flows through an inner tube and the coating material, which should be immiscible with core material, flows through an annular tube around it. As the head rotates or vibrates, the core and coating material emerge from the orifices at the end of the tubes and break up into spherical drops due to surface tension forces. These are then solidified in a bath by using heat or suitable chemical reactions [13,31]. There is no report of PCM encapsulation via this method, although it seems feasible.

2.4. Vibrational nozzle

Core–shell encapsulation or microgranulation (matrix-encapsulation) is usually conducted using a laminar flow through a nozzle with an additional vibration of the nozzle or the liquid. The vibration leads to very uniform droplets [32]. This method has not been used for PCM microencapsulation, although form-stable PCM composites were prepared in a similar way but without vibration [6–9,33–35].

2.5. Spray drying

Spray drying encapsulation is a low-cost commercial process which is done by spraying an intimate mixture of core and shell

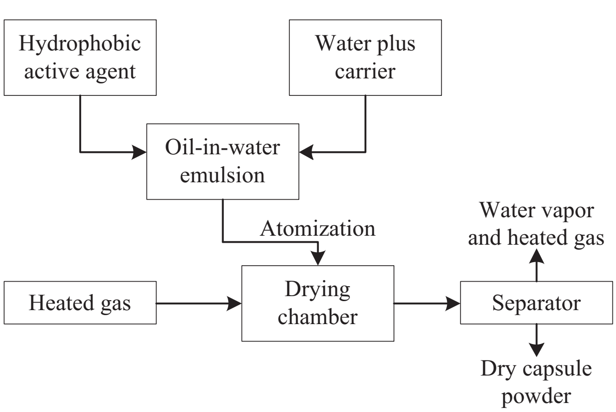


Fig. 3. Flow diagram of a typical spray drying encapsulation process [31].

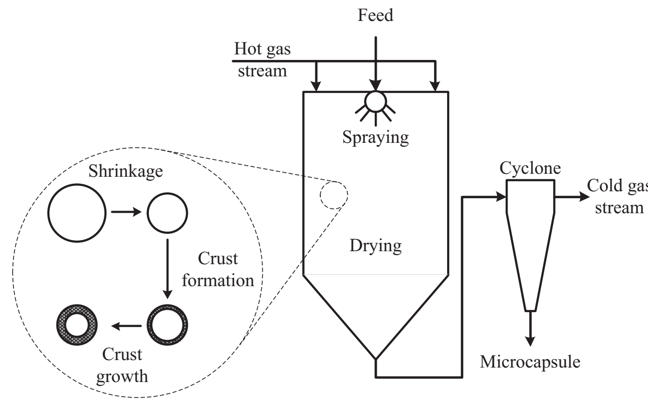


Fig. 4. Schematic representation of the spray drying equipment.

material into a heated chamber where rapid evaporation occurs to thereby produce microcapsules (Fig. 3). This technique comprises the following steps [36] as illustrated in Fig. 4:

1. Spraying the feed solution or emulsion in small droplets by means of an atomizer.
2. Placing the previous dispersion in contact with the gas stream at the temperature necessary for the complete evaporation of the solvent.
3. Separating the solid particles carried by the gas phase by means of cyclones and/or filters.

Usually the microcapsules obtained by this method are of polynuclear or matrix type. Agglomerated and uncoated particles are common problems of this rapid microencapsulation method [13]. On the other hand, this technique can be easily scaled-up and the production of homogeneous microcapsules with desired particle size is achievable by designing proper atomizer [37].

Limited researchers have produced MEPCMs via this method successfully. Hawlader et al. [38] prepared MEPCMs containing paraffin-wax as core material and gelatine/acacia as shell materials by complex coacervation and spray drying methods. They investigated the influence of different parameters on the characteristics and performance of a MEPCM in terms of encapsulation efficiency, and energy storage capacity. SEM and DSC tests show spherical capsules with a uniform size distribution and a high energy storage density.

Fei et al. [39] produced microcapsules with *n*-octadecane (C18) core and a titania shell by a rapid aerosol process with a hydrothermal post-treatment. While the highest loading of core material was up to 50–60% in literature [13], they had a high core loading of nearly 80% with an enthalpy 92–97 J/g. The final capsules had diameters 0.1–5.0 μm with two structures of dense or hollow spheres.

Fig. 5 shows the spray dryer equipment used by Borreguero et al. [37] to encapsulate the paraffin Rubitherm®RT27 with and without carbon nanofibers (CNFs) using low density polyethylene–ethylvinylacetate (LDPE–EVA) as a polymer shell. Characteristics of microcapsules containing this PCM were dependent on the location in which they were collected in the spray dryer (i.e., the product collector and drying chamber) and the SEM results show a minimum average particle size of 3.9 μm. Besides, the thermal analysis indicated an encapsulation yield of 49% and a possible enhancement of the thermal conductivity and stiffness of the microcapsules using the CNFs while the heat storage capacity was maintained constant. Fig. 6 illustrates a SEM image of the produced MEPCM.

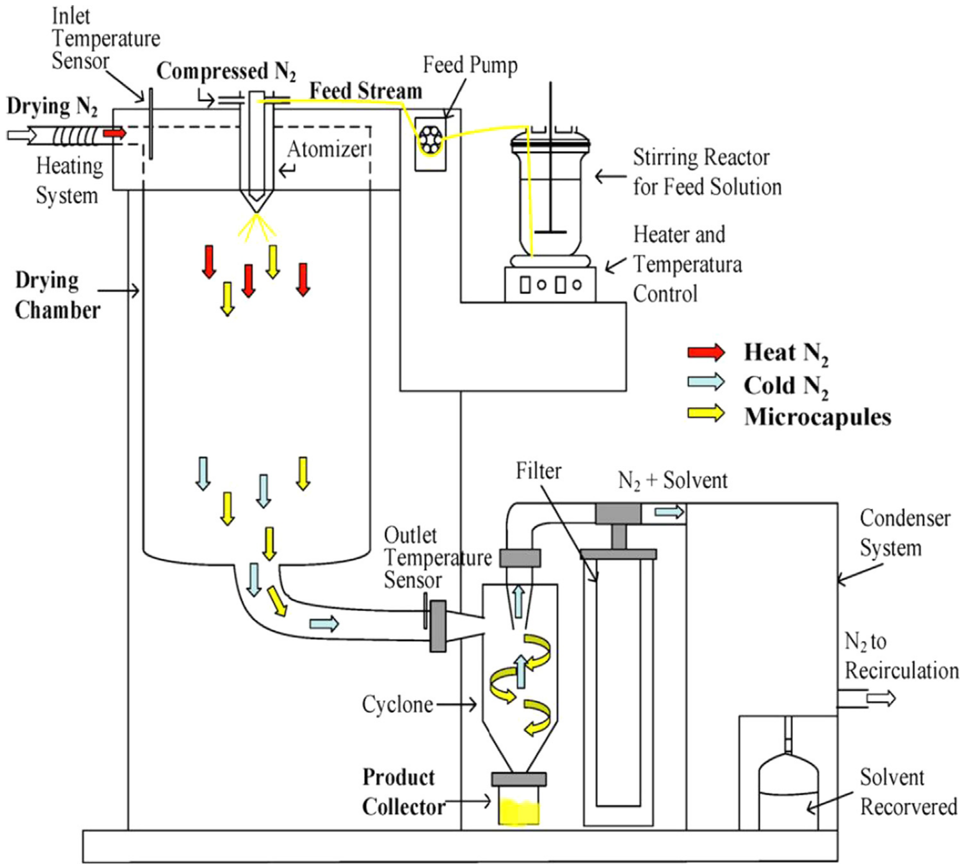


Fig. 5. Fluidized bed used by [37].

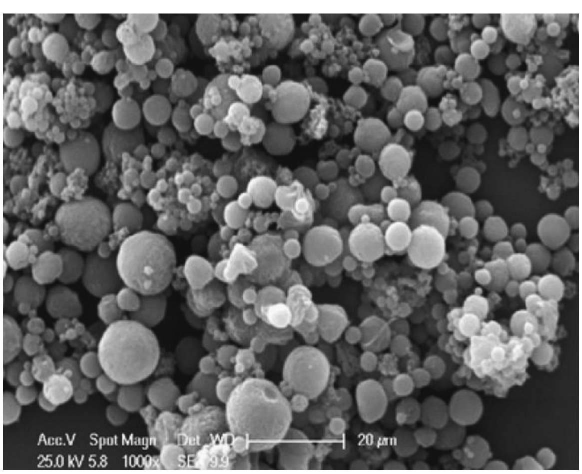


Fig. 6. SEM photograph of prepared microcapsule [37].

2.6. Solvent evaporation

Emulsification of polymer volatile organic solvent in water followed by solvent removal is called "solvent evaporation" [26]. This technique is widely used in pharmaceutical industries and carried out in a liquid manufacturing vehicle (LMV). Initially a coating polymer solution is prepared by dissolving the coating polymer material in a volatile solvent which is immiscible in LMV. Then, depending on the hydrophobicity or hydrophilicity of the core material, it is dissolved or dispersed in the coating polymer solution, respectively. The mixture is added to the LMV phase with continued agitation until the solvent is partitioned into the aqueous phase and evaporated. Here the coat material shrinks around the core material and results in hardened microspheres. Detailed description of this technique is given in [40].

Table 1 summarizes the advantages and disadvantages of physical methods and express if the method is suitable for PCM encapsulation or not.

3. Physic-chemical methods

In these methods, a physic-chemical process, i.e. gelation or coacervation, leads to a solid and stable particle.

3.1. Ionic gelation

Ionic gelation method is widely used in pharmaceutical industry especially in drug delivery systems and has not been evaluated for encapsulating of PCMs yet. This method is based on the ability of polyelectrolytes to crosslink in the presence of multivalent counter ions such as Ca^{2+}, Ba^{2+} and Al^{3+} to form hydrogels [24]. For example, ionic gelation of alginate and calcium ion would leads to the calcium alginate (CaAlg) microcapsules [22].

3.2. Coacervation

The term coacervation was originated from the Latin word "acervus", meaning "heap" [23]. The process of coacervation may be either simple or complex. Simple coacervation is the result of the interaction of a dissolved polymer with a low-molecular substance. Complex coacervation occurs through the interaction of two polymers whose macromolecules bear opposite charges.

Table 1
Physical microencapsulation methods [27,115,116].

Technique	Advantages	Disadvantages	Applicable to MEPCM production
Pan coating	• Low-cost equipment	• Difficult to control • High skill level required	No
Air-suspension coating	• Low cost • Higher production volume	• High skill level required • Agglomeration of particles	No
Centrifugal extrusion	• Suitable for bioencapsulation	• High temperature	Yes
Vibrational nozzle	• High yields of production • Easy to scale-up	• High temperature	Yes
Spray drying	• Equipment and know-how widely available • Versatile • Easy to scale-up	• High temperature • Agglomeration of particles • Remaining uncoated particles	Yes
Solvent evaporation	• Low cost	• Lab scale production	Yes

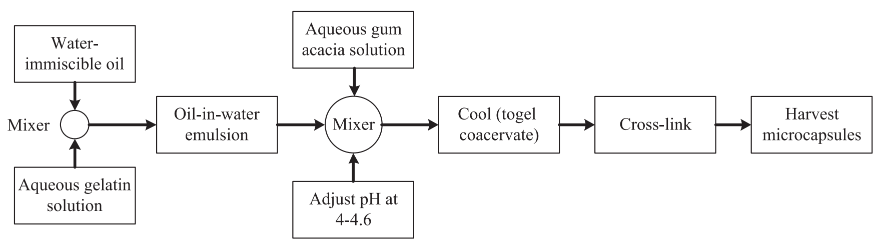


Fig. 7. Flow diagram of a typical complex coacervation encapsulation process [31].

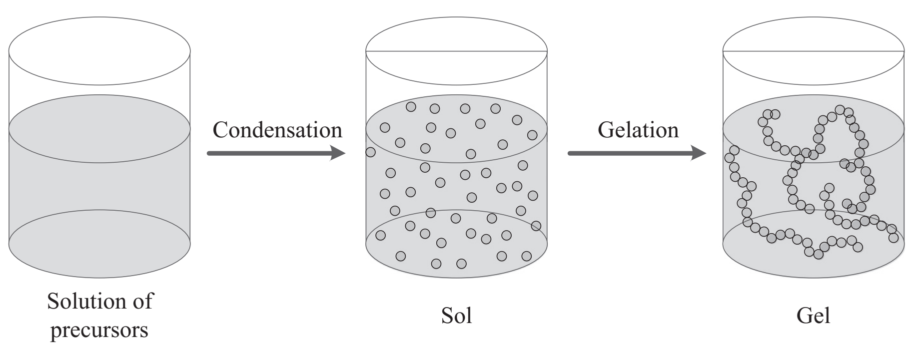


Fig. 8. Scheme of a sol-gel process [115].

The first step in complex coacervation method is the preparation of the emulsion via dispersion of core material (usually oil) into an aqueous polymer solution. Then the deposition of shell material onto the core particles is occurred by adding the second aqueous polymer solution followed by the addition of salt or by changing the pH, temperature, or by dilution of the medium. The final step is the stabilization of the microcapsules by crosslinking, desolvation or thermal treatment [13].

Fig. 7 shows the flow diagram of a typical complex coacervation technique which is usually used for encapsulation of PCMs. After that the core material is dispersed in an aqueous gelatine solution at a temperature range at which the wall material solution is liquid, gum acacia, a polyanion or negatively charged polymer, is added to the gelatine solution. The process is followed by adjusting the pH and concentration of polymer so that a liquid complex coacervate formed. Once the liquid coacervate is formed, the system is cooled to gel coated. The final step is hardening of microcapsules by using formaldehyde or glutaraldehyde [41].

Hawlader et al. [38,42] prepared microencapsulated paraffin wax by complex coacervation technique and studied the influence of core-to-coating mass ratio on its characteristics and performance such as hydrophilicity, energy storage capacity, and size distribution. They used gelatine/gum acacia as a shell material and the processing conditions were optimized based on the response surface method (RSM). In different studies, Hawlader et al. [43] performed both experiments and simulation to investigate the characteristics of MEPCMs prepared by complex coacervation method. Also microencapsulation of Rubitherm® RT 27, a paraffin wax based material, was successfully done by Bayés-García et al. [44] via complex coacervation method. They used two different coacervates as shell composition (sterilized gelatine/acacia gum and agar-agar/acacia gum) and the SEM results show an average

Table 2
Physic-chemical microencapsulation methods [24,115].

Technique	Advantages	Disadvantages	Applicable to MEPCM production
Ionic gelation	• Low cost • Low temperature	• High wall permeability	Yes
Coacervation	• Versatile • Efficient control of the particle size	• Aldehyde as hardener • Difficult to scale-up • Agglomeration	Yes
Sol-gel	• Inorganic shell with high thermal conductivity	• Still under research	Yes

diameter of 12 μm for the SG/AG shell and smaller capsules for the AA/AG shell, where nanocapsules were also observed. They obtained encapsulation ratios of 49% and 48% for the SG/AG and AA/AG shells, respectively. Encapsulation ratio, R is defined as follow [17]:

$$R = \frac{\Delta H^{\mathrm{m}}_{\mathrm{MEPCM}}}{\Delta H^{\mathrm{m}}_{\mathrm{PCM}}} \times 100 \tag{1}$$

Also, the encapsulation ratio (sometimes referred to encapsulation efficiency, η) may define as follow [17]:

$$\eta = \frac{\Delta H^{\mathrm{m}}_{\mathrm{MEPCM}} + \Delta H^{\mathrm{s}}_{\mathrm{MEPCM}}}{\Delta H^{\mathrm{m}}_{\mathrm{PCM}} + \Delta H^{\mathrm{s}}_{\mathrm{PCM}}} \times 100 \tag{2}$$

In addition to the paraffin wax used as the core material, coco fatty acid mixture can also be a candidate for MEPCM. Özonur et al. [41] used inexpensive natural coco fatty acid as the core material, and several alternatives for the capsule wall material were tried by the simple and complex coacervation techniques. They concluded that gelatine/gum acacia is the best capsule wall material for coco fatty acid mixture. Due to the cheap materials used in this MEPCM, it is probably one of the cheapest MEPCM. Simple coacervation method was successfully used by Konuklu et al. [45] to encapsulate the caprylic acid with different wall materials, including urea/formaldehyde, melamine/formaldehyde, and urea–melamine/formaldehyde resins. They concluded that the urea/formaldehyde resin is the best capsule wall material for caprylic acid.

Butstraen and Salaün [46] established the optimum parameters of the encapsulation process of acacia gum/chitosan microcapsules containing a blend of triglycerides (Miglyol 812 N) synthesized by complex coacervation. Their results indicated that the optimum conditions are pH=3.6, weight ratio of chitosan to acacia gum mixture of 0.25, the phase volume ratio of the dispersed and continuous phases of 0.1, and an emulsion time of 15 min at 11,000 rpm.

Outlast® and ComforTemp® are the trade names of a variety of outdoor apparel products, such as ski wear, hunting clothing, boots, gloves, and ear warmers, which incorporate MEPCMs into fabrics or foams [47]. Several investigators have worked on preparation of MEPCMs for using in thermoregulated textiles. Onder et al. [48] successfully encapsulated paraffin waxes suitable for textile applications through complex coacervation of gelatine/gum acacia mixture, in order to investigate their performances when integrated into woven fabrics by coating. They concluded that the complex coacervation of gelatine/gum acacia to encapsulate paraffin waxes and their incorporation into woven fabrics by coating is recommended for use with textile products. Deveci and Basal [49] successfully prepared MEPCM by complex coacervation of silk fibroin and chitosan (with an antibacterial activity). Their study confirmed that the biopolymer SF/CHI wall system can be utilized to encapsulate a PCM.

Some literature uses the name "phase separation" instead of "coacervation" [22,24]. *n*-Tetradecane was successfully encapsulated by polymethyl methacrylate (PMMA), polystyrene (PS) and blend of them [50], and acrylonitrile–styrene (AS), acrylonitrile–styrene–butadiene (ABS) and polycarbonate (PC) [51], via phase separation method.

3.3. Sol-gel method

The sol-gel process may be described as the polycondensation reactions of a molecular precursor in a liquid phase to form a colloidal solution (sol) which is subsequently converted to an oxide network (gel) (Fig. 8).

The inorganic encapsulation of PCM (*n*-pentadecane) with silica shell via a combination of O/W emulsion technique with the sol-gel method was studied by Wang et al. [52] for the first time. SEM results confirmed the production of spherical microcapsules in the 4–8 μm size range. Fang et al. [11] and Zhang et al. [53] also successfully synthesized and characterized the microencapsulated paraffin with SiO_2 shell via sol-gel method. They both achieved an encapsulation ratio of paraffin of more than 85%. The high thermal conductivity of the silica shell may improve the rate of heat storage and release.

Stearic acid is a saturated fatty acid with the melting point of 56.1 °C. Microencapsulated stearic acid with SiO_2 shell material was prepared using sol-gel method by Chen et al. [54]. A great encapsulation ratio of 90.7% was reported. In another study, Chen et al. [55] successfully microencapsulated and characterized paraffin wax with SiO_2 shell material. Their DSC results indicated that the microcapsules melted at 58 °C with a latent heat of 156.9 J/g.

Advantages and disadvantages of physic-chemical methods are summarized in Table 2.

4. Chemical methods

The most important chemical technique used for microencapsulation of PCMs is the in situ polymerization, which includes interfacial, emulsion and suspension polymerization, although there are some other methods [56,57]. Fig. 9 illustrates and compares the different types of polymerization methods used to form PCM microcapsules that are discussed below in more details.

4.1. Interfacial polymerization

Wall formation at this technique is the result of a rapid polymerization of hydrophilic and lipophilic monomers at the interface of an oil-in-water emulsion. As illustrated in Fig. 10, the solution containing lipophilic reactant X in the core material is emulsified in an aqueous phase that contains an emulsifier. At that point, hydrophilic reactant Y is added to the aqueous phase thereby originating interfacial polymerization and shell formation. Once reaction is initiated, the wall that forms becomes a barrier to diffusion and eventually begins to limit the rate of the interfacial

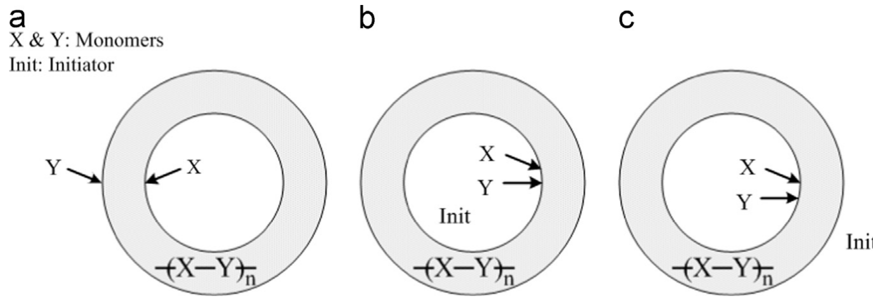


Fig. 9. Schematic diagrams that illustrate the difference between the chemical microencapsulation methods: (a) interfacial polymerization, (b) suspension polymerization, and (c) emulsion polymerization.

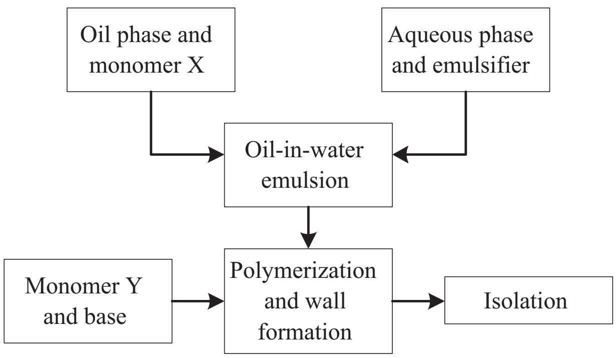


Fig. 10. Flow diagram of a typical interfacial polymerization encapsulation process [31].

polymerization reaction and influences morphology and uniformity of the capsule shell. The base, as an acid scavenger, is added to the solution if the reactant X is an acid chloride.

One of the early attempts to model microencapsulation via interfacial polymerization has been done by Yadav et al. [58]. Their model was based on the diffusion of the hydrophilic monomer HMDA (hexamethylene-1,6-diamine) through the polymeric shell followed by a polymerization reaction with the hydrophobic monomer HMDI (hexamethylene-1,6-diisocyanate) at the inner surface. The results indicated that the time of encapsulation is approximately proportional to the size and the square of size in the kinetically controlled and diffusion-controlled regimes, respectively. Another study of Yadav et al. [59] indicated that the shell thickness and permeability can be changed by changing of crystallinity of the polymer.

There are numerous reports that engaged polyurea (PU) as a shell material for encapsulation of different core materials such asmigrin oil [60], ovalbumin [61], *n*-octadecane [62–67], *n*-hexadecane [68], *n*-eicosane [69], and butyl stearate [70], using interfacial polymerization method. Siddhan et al. [64] microencapsulated *n*-octadecane using core and bulk monomers as toluene-2,4-diisocyanate (TDI) and diethylenetriamine (DETA), respectively. The oil phase was formed by dissolving TDI and *n*-octadecane in cyclohexane. They used Nonyl Phenol (NP-9.5) as surfactant. The effect of various encapsulation parameters was investigated to increase the core content, encapsulation efficiency, and stability of microcapsules to hot water wash. Lone et al. [71] fabricated highly monodisperse PU microcapsules containing *n*-octadecane using a microfluidic approach illustrated in Fig. 11. Tuning the flow rate of either the continuous or discontinuous phase was the key parameter in controlling the average diameter and morphology of the produced MEPCM.

Urea–formaldehyde polymer is another shell material used for encapsulation of different core materials via interfacial polymerization method. The possibility of changing the degree of crystallinity of urea microcapsules through the choice of preparation conditions makes it feasible to control the core release behavior for different applications. Park et al. [72] successfully prepared urea–formaldehyde microcapsules containing fragrant lemon oil. Three PCMs (*n*-pentadecane, *n*-eicosane, and a paraffin wax) were also encapsulated using urea–formaldehyde shell by Tseng et al. [73].

Gao et al. [74] enhanced the sealing performance and thermal stability of microcapsules by means of joining PU and melamine formaldehyde (MF) resin. Su et al. [75] used melamine-formaldehyde resin as the shell material and prepared different types of microcapsules via interfacial polymerization method. They evaluated the mechanical properties of the microcapsules by pressing the microcapsules between two glass plates and observing the surface morphological structure change by means of SEM. They found a yield point of about 1.1×10^5 Pa for a mass ratio of core to shell material equal to 3:1. As Fig. 12 shows, when the compression was increased beyond this point the microcapsules showed plastic behavior. Khakzad et al. [76] investigated the influence of stabilizer type and amount, surfactant amount, and homogenization conditions (i.e. homogenization speed and time) on the final particle size, morphology, and thermal properties of the microcapsules, containing hexadecane core and melamine formaldehyde shell. They concluded that using PVA with higher molecular weight as a stabilizer could lead to microcapsules with appropriate morphology and thermal properties. The stabilizer amount of 1 wt%, surfactant amount of 4 wt% (80:20 mixture of sodium dodecylsulphate (SDS)/Triton X-100), homogenization speed of 6000 rpm, and homogenization time of 20 min were found to produce optimum condition.

Wei et al. [77] successfully synthesized a new type of polyamide (PA)-shell MEPCM containing paraffin by interfacial polymerization technique. The prepared MEPCM could disperse in water and organic solvent easily and showed good thermal and chemical stability.

4.2. Suspension polymerization

This technique of PCM encapsulation is characterized by the suspension of the water immiscible reaction mixture as droplets in the aqueous continuous phase [78]. These droplets are formed through vigorous agitation of the mixture and dissolution of stabilizers in aqueous phase. Then, polymerization is initiated at the desired temperature until completion. The average diameter of the resulting particles ($\bar{d}$ [m]) is affected by changing the stirring speed (N [m s^{-1}]), volume fraction of monomer phase (R), stabilizer concentration (C_s [kg m^{-3}]), viscosity of droplet (ϑ_d [cP]), and viscosity of suspension medium (ϑ_m [cP]) according to the following formula [79,80]:

$$\bar{d} = k\frac{D_v R \vartheta_d \varepsilon}{D_s N^2 \vartheta_m C_s} \tag{3}$$

where k = parameters such as apparatus design, type of stirrer, self-stabilization; D_v (m) is the diameter of the vessel; D_s (m) is the

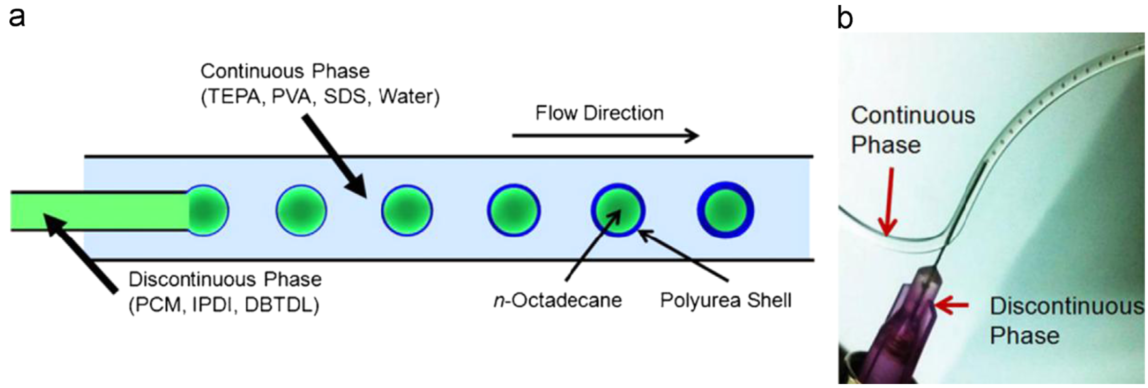


Fig. 11. (a) Schematic diagram of the fabrication of monodispersed microcapsules and (b) photograph of O/W PCM droplets produced at the tubular junction [71].

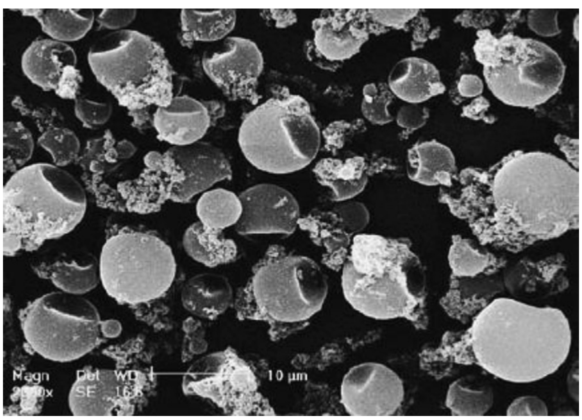


Fig. 12. SEM photograph of microcapsules after compression [75].

diameter of the stirrer; and ε (N m^{-1}) = interfacial tension between the two immiscible phases.

Sánchez at al. [81] successfully encapsulated different non-polar PCMs such as PRS® paraffin wax, tetradecane, Rubitherm®RT27, Rubitherm®RT20, and nonadecane with a polymer shell of polystyrene by suspension polymerization method. They concluded that it is not possible to encapsulate polar PCMs (polyglycols) because of their hydrophilic nature. They also studied the influence of operating conditions such as reaction temperature, stirring rate, and mass ration of PRS® paraffin wax to styrene on the properties of MEPCMs (thermal storage capacity, particle size distribution and morphology) [82]. In another study, Sánchez at al. [83] used the Shirasu porous glass (SPG) membrane with pore sizes of 5.5 μm to produce a narrow microcapsules size distribution. They investigated the effect of different parameters such as the ratios of PRS® paraffin wax/styrene, polyvinylpyrrolidone (stabilizer)/styrene, and water/styrene on the particle size distribution and thermal energy storage of microcapsules prepared via suspension polymerization method. Afterwards Sánchez-Silva et al. [84] successfully designed a pilot plant for MEPCM production via suspension polymerization technique with a similar particle size and PCM content to those obtained in the laboratory.

n-Pentadecane was encapsulated into the methyl methacrylate (MMA) by Taguchi et al. [85] via the suspension polymerization method. Sánchez-Silva et al. [86] succeeded in enhancing the average energy storage capacity of the microcapsules containing PRS® paraffin wax by means of a copolymer of MMA and styrene as the shell material instead of polystyrene. This was due to the higher reactivity and polarity of MMA compared to styrene.

Chang et al. [87] prepared microcapsules with polymethyl methacrylate (PMMA) network-silica hybrid as the shell material and *n*-octadecane as the core material based on suspension polymerization. They used three kinds of mixing solutions of PCM and MMA to prepare the suspension solution before polymerization: (a) mixing PCM and monomer directly; (b) introducing PCM, then introducing monomers; and (c) introducing PCM, then introducing monomers with prepolymer. The results indicated that the most effective method to prepare microcapsules is through the use of prepolymer solutions and the addition of tetraethoxysilane (TEOS) into the prepolymer solution would result in microcapsules with higher latent heat (ΔH = 151 J/g) than those without TEOS (ΔH = 88.3 J/g).

You et al. [88] added MEPCMs (*n*-octadecane) with styrene–divinybenzene copolymer shell in foaming system directly and PU foams with increased enthalpy were produced. In another study they investigated the influence of different parameters on microencapsulation of *n*-octadecane with styrene–divinybenzene copolymer shell [89]. Incorporating MEPCMs obtained by suspension polymerization in gypsum wallboard to increase its energy storage capacity was studied by Borreguero et al. [90]. They improved the thermal insulation capacity of the gypsum by addition of microcapsules containing Rubitherm® RT27.

Li et al. [91] encapsulated *n*-octadecane with different copolymer shells by suspension polymerization. They investigated the influence of initiator type (i.e., water-soluble initiator APS and oil-soluble initiator AIBN) and concluded that the oil-soluble initiator is more suitable for the microencapsulation of *n*-octadecane. In another study, *n*-octadecane that contained homodispersed polypyrrole (PPy) particles was encapsulated with a PMMA/PAMA copolymer shell [92]. They succeeded in eliminating the supercooling from the MEPCM by adding 4–14 wt% PPy in the core, while PPy had no influence on the morphology and particle distribution of the microcapsules.

A new hybrid shell of polymer/SiO_2 was used by Yin et al. [93] to encapsulate dodecanol as a core material. They successfully eliminated the surfactant or dispersant material by using the organically modified SiO_2 particles.

Microencapsulation of hydrated salt PCMs is difficult because of their water-solubility. Recently, Huang et al. [94] prepared microcapsules loaded by $Na_2HPO_4 \cdot 7H_2O$ via the suspension copolymerization-solvent volatile method. They used modified PMMA as coating polymer and achieved mean diameter and latent heat of melting of around 6.8 μm and 150 J/g, respectively. Their TGA showed a weight loss of 10% in the temperature range from 30 to 84 °C, which indicated that the encapsulated salt hydrate suffered a water loss. Afterward they succeeded in microencapsulation of $Na_2HPO_4 \cdot 12H_2O$ with the MMA crosslinked with ethyl acrylate (EA) [95]. Meanwhile, they produced urea–formaldehyde (UF) resin microcapsules contained $Na_2HPO_4 \cdot 12H_2O$. They concluded that the weight loss of microcapsule with the UF shell is lower than that of the PMMA shell.

4.3. Emulsion polymerization

In emulsion polymerization, unlike suspension polymerization, the initiator is soluble in the aqueous phase and the monomer is emulsified in the polymerization medium by the aid of a surfactant. As illustrated in Fig. 13, the monomer is distributed between droplets emulsion, surfactant micelles, and scarcely the water phase. Since the initiator is present only in the aqueous phase, the starting point for the polymerization reaction is in this phase (i.e., outside the droplets and micelles) and subsequently extends to the micelles. The average diameter of the resulting particles is mainly affected by the fraction of the monomer molecularly dissolved in the aqueous phase. Besides, it is influenced by the emulsifier concentration, initiator concentration, and polymerization temperature [79].

Baek et al. [96] successfully prepared PCM (*n*-octadecane) nanocapsules by emulsion polymerization of styrene. They used alkali-soluble resin (ASR) of poly(ethylene-*co*-acrylic acid) (EAA) and poly (styrene-*co*-acrylic acid) (SAA) as surfactant and water-soluble

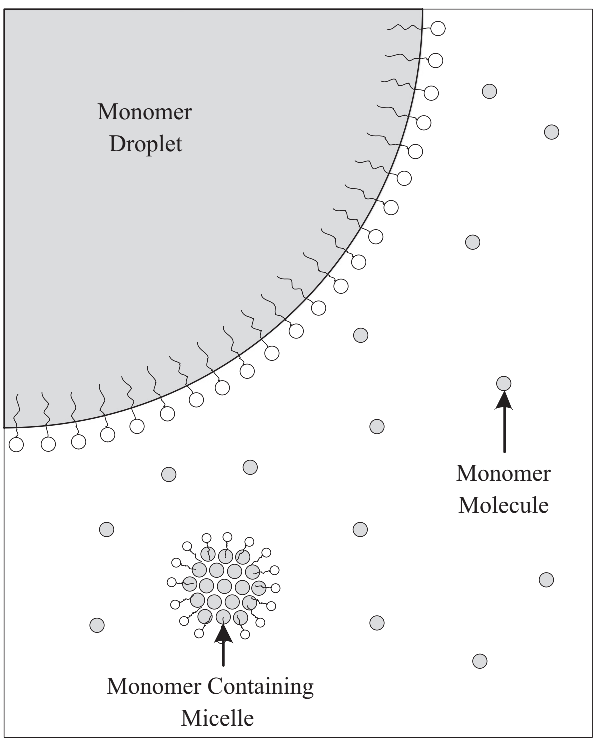


Fig. 13. Schematic representation of early stages of emulsion polymerization [79].

potassium persulfate as initiator. The maximum encapsulation ratio of 66.7% was achieved through the use of SAA surfactant.

Alkan and their colleagues carried out a number of studies in the preparation of microencapsulated PCM by emulsion polymerization using docosane [97], *n*-octacosane [98], *n*-hexadecane [99,100], and *n*-heptadecane [101] as core material and PMMA resin as shell materials. They characterized their properties such as particle size distribution, chemical characterization, latent heat, and thermal stability using SEM, FT-IR, DSC, and TGA. Based on all results, they concluded that the PMMA/PCM microcapsules have good energy storage potential. They also indicated that the type of alkane and cross-linker agent (e.g., glycidylmethacrylate, allyl methacrylate, and ethylene glycol dimethacrylate) has a great influence on the encapsulation ratio, particle size, and structure of microcapsules. The particles prepared using *n*-hexadecane as a core material and glycidyl methacrylate or ethylene glycol dimethacrylate as a cross-linker agent had higher encapsulation ratio (i.e., 62% compared to 28–43%), more spherical surface, and smaller size.

The ultraviolet (UV) light is a useful tool for initiating polymerization. One of the most important advantages of the UV initiated polymerizations is the temperature independency of the radical flux, whereas a high temperature is necessary in chemical initiation [102]. Ma et al. [103] successfully prepared paraffin microcapsules with PMMA shell through an emulsion polymerization, which were initiated by UV irradiation in the presence of a water-soluble photoinitiator of Photocure® 2959.

Alay et al. [104] produced microencapsulated *n*-hexadecane with poly(butyl acrylate) (PBA) by using allyl methacrylate, ethylene glycol dimethacrylate, and glycidyl methacrylate as cross-linkers. The results indicated that the microcapsules prepared using ethylene glycol dimethacrylate cross-linker had the highest heat capacity.

5. Nanoencapsulation

Nowadays, the technological developments made it real to encapsulate PCM at nanoscale. The size of PCM capsule plays an important role and could expand the frontiers of encapsulated PCM applications. Nanocapsules are structurally more stable than microcapsules as it was shown by Sukhorukov et al. [105]. They observed significantly smaller deformation for the 10 nm size capsules compared to those of 10 μm size while the same force applied. In some fields, especially in MPCS, MEPCMs are not appropriate for long-term circulation, because they could easily fracture in the course of flow and during pumping. They also increase the fluid's viscosity [106–108]. Therefore, the development of nanoencapsulated PCM (NEPCM) is inevitable.

Table 3
Relevance of microencapsulation techniques of PCMs.

Microencapsulation process	Particle size range (μm)	Encapsulation ratio (%)	Common shell material	Common PCM type
Spray drying	0.1–5000	38–63	LDPE/EVA Gelatin/acacia gum Titania	Paraffin wax
Coacervation	2–1200	6–68	Gelatin/acacia gum SF/CHI	Paraffin wax Fatty acid
Sol-gel	0.2–20	30–87	Silica	Paraffin wax
Interfacial polymerization	0.5–1000	15–88	PU Urea/formaldehyde Melamine/formaldehyde	Paraffin wax
Suspension polymerization	2–4000	7–75	Polystyrene PMMA MMA/St	Paraffin wax
Emulsion polymerization	0.05–5	14–67	Polystyrene PMMA	Paraffin wax

There are some works that synthesized NEPCM by using different methods. One of the most used methods for the production of NEPCM is the emulsion polymerization technique [96,106,108–111] while the other methods such as interfacial polymerization [112–114] and sol-gel [107] methods have also been used. Wang et al. [102] nanoencapsulated eicosanoic–stearic acid eutectic with PMMA shell by UV initiated emulsion polymerization technique and investigated the influence of various parameters on thermal properties and particle size distribution of final NEPCM. They concluded that nanoencapsulation would dramatically reduce the supercooling problem of PCMs.

6. Further research areas

As reviewed, efforts were devoted to produce variety of MEPCMs having different core and shell materials and variable thermal and mechanical properties which are suitable for different latent heat thermal energy storage systems. However, rigorous testing of the produced MEPCMs is necessary to insure their quality. Most of these PCM microcapsules, including those manufactured commercially have not been thoroughly tested. Suggestions for the future works may include the following:

- Long term instability; especially when it is used to enhance heat transfer efficiency of a fluid in a pumping cycle or in buildings.
- Supercooling; it is a major obstacle to the industrial application of MEPCMs, since most PCMs tend to supercool when encapsulated.
- A standard mechanical testing for microcapsules is needed, since most of the produced MEPCMs are not tested for leakage.
- Hydrated salt encapsulation; since these salts, which have high latent heat, can degrade dramatically when they lose or gain water.
- More work is needed on UV initiated polymerization during PCM encapsulation. This will allow carrying encapsulation at lower temperatures, which will improve the quality of the microcapsules.

7. Conclusions

Microencapsulation technology is used to prepare MEPCM, as a new kind of thermal energy storage composite material. The preparation methods that reviewed were classified into three categories, i.e. physical, physic-chemical, and chemical methods. The selection of these microencapsulation techniques is highly dependent on the specifications of microcapsules; the required capsule size, materials of the core and shell, thickness of the microcapsule shell, thermal and mechanical properties of the capsule, etc. Consequently the process must be custom-tailored in order to provide a satisfactory outcome. The most common methods described in the literature for MEPCM production are interfacial polymerization, suspension polymerization, coacervation, emulsion polymerization, and spray drying. An overview of relative particle size range, encapsulation ratio, and core and shell materials used in these microencapsulation techniques is provided in Table 3. Instability and supercooling of MEPCMs still need further investigations and would be overcome by NEPCMs and multiphase core materials, respectively.

References

[1] Farid MM, Khudhair AM, Razack SAK, Al-Hallaj S. A review on phase change energy storage: materials and applications. Energy Convers Manag 2004;45: 1597–1615.
[2] Khudhair AM, Farid MM. A review on energy conservation in building applications with thermal storage by latent heat using phase change materials. Energy Convers Manag 2004;45:263–75.
[3] Zalba B, Marin J, Cabeza L, Mehling H. Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. Appl Therm Eng 2003;23:251–83.
[4] Sharma A, Tyagi VV, Chen CR, Buddhi D. Review on thermal energy storage with phase change materials and applications. Renew Sustain Energy Rev 2009;13:318–45.
[5] Hong Y, Xin-shi G. Preparation of polyethylene-paraffin compound as a form-stable solid–liquid phase change material. Sol Energy Mater Sol Cells 2000;64:37–44.
[6] Cai Y, Song L, He Q, Yang D, Hu Y. Preparation, thermal and flammability properties of a novel form-stable phase change materials based on high density polyethylene/poly(ethylene-*co*-vinyl acetate)/organophilic montmorillonite nanocomposites/paraffin compounds. Energy Convers Manag 2008;49:2055–62.
[7] Sarl A. Form-stable paraffin/high density polyethylene composites as solid-liquid phase change material for thermal energy storage: preparation and thermal properties. Energy Convers Manag 2004;45:2033–42.
[8] Sarl A, Karaipekli A. Preparation, thermal properties and thermal reliability of palmitic acid/expanded graphite composite as form-stable PCM for thermal energy storage. Sol Energy Mater Sol Cells 2009;93:571–6.
[9] Song G, Ma S, Tang G, Yin Z, Wang X. Preparation and characterization of flame retardant form-stable phase change materials composed by EPDM, paraffin and nano magnesium hydroxide. Energy 2010;35:2179–83.
[10] Zhang YP, Lin KP, Yang R, Di HF, Jiang Y. Preparation, thermal performance and application of shape-stabilized PCM in energy efficient buildings. Energy Build 2006;38:1262–9.
[11] Fang G, Chen Z, Li H. Synthesis and properties of microencapsulated paraffin composites with SiO2 shell as thermal energy storage materials. Chem Eng J 2010;163:154–9.
[12] Tyagi VV, Kaushik SC, Tyagi SK, Akiyama T. Development of phase change materials based microencapsulated technology for buildings: a review. Renew Sustain Energy Rev 2011;15:1373–91.
[13] Ghosh SK. Functional Coatings and microencapsulation: a general perspective. Functional coatings. Wiley-VCH Verlag GmbH & Co. KGaA; 2006; 1–28.
[14] Chen Z, Fang G. Preparation and heat transfer characteristics of microencapsulated phase change material slurry: a review. Renew Sustain Energy Rev 2011;15:4624–32.
[15] Sabbah R, Farid MM, Al-Hallaj S. Micro-channel heat sink with slurry of water with micro-encapsulated phase change material: 3D-numerical study. Appl Therm Eng 2009;29:445–54.
[16] Zhang P, Ma ZW, Wang RZ. An overview of phase change material slurries: MPCS and CHS. Renew Sustain Energy Rev 2010;14:598–614.
[17] Salunkhe PB, Shembekar PS. A review on effect of phase change material encapsulation on the thermal performance of a system. Renew Sustain Energy Rev 2012;16:5603–16.
[18] Kwak K, Kim C. Viscosity and thermal conductivity of copper oxide nanofluid dispersed in ethylene glycol. Korea–Australia Rheol J 2005;17:35–40.
[19] Azari A, Kalbasi M, Rahimi M. Numerical study on the laminar convective heat transfer of alumina/water nanofluids. J Thermophys Heat Transf 2013;27:170–3.
[20] Boh B, Šumiga B. Microencapsulation technology and its applications in building construction materials Tehnologija mikrokapsuliranja in njena uporaba v gradbenih materialih. RMZ–Mater Geoenviron 2008;55:329–44.
[21] Zhao CY, Zhang GH. Review on microencapsulated phase change materials (MEPCMs): fabrication, characterization and applications. Renew Sustain Energy Rev 2011;15:3813–32.
[22] Huang H-J, Yuan W-K, Chen XD. Microencapsulation based on emulsification for producing pharmaceutical products: a literature review. Dev Chem Eng Miner Process 2006;14:515–44.
[23] Jyothi NVN, Prasanna PM, Sakarkar SN, Prabha KS, Ramaiah PS, Srawan G. Microencapsulation techniques, factors influencing encapsulation efficiency. J Microencapsul 2010;27:187–97.
[24] Yeo Y, Baek N, Park K. Microencapsulation methods for delivery of protein drugs. Biotechnol Bioprocess Eng 2001;6:213–30.
[25] Salaün F. The manufacture of microencapsulated thermal energy storage compounds suitable for smart textile. In: Marco Aurelio Dos Santos B, editor. Developments in heat transfer; 2011.
[26] Poncelet D. Microencapsulation: fundamentals, methods and applications. In: Blitz J, Gun'ko V, editors. Surface chemistry in biomedical and environmental science. Netherlands: Springer; 2006. p. 23–34.
[27] Venkatesan P, Manavalan R, Valliappan K. Microencapsulation: a vital technique in novel drug delivery system. J Pharm Sci 2009;1:26–35.
[28] Wurster DE. Air-suspension technique of coating drug particles. A preliminary report. J Am Pharm Assoc 1959;48:451–4.
[29] Werner SRL, Jones JR, Paterson AHJ, Archer RH, Pearce DL. Air-suspension particle coating in the food industry: part I – state of the art. Powder Technol 2007;171:25–33.
[30] Cheng SY, Yuen CWM, Kan CW, Cheuk KKL. Development of cosmetic textiles using microencapsulation technology. Res J Text Appar 2008;12:41–51.
[31] Thies C. Microencapsulation. Kirk-Othmer encyclopedia of chemical technology. John Wiley & Sons, Inc; 2000.
[32] Heinzen C, Berger A, Marison I. Use of vibration technology for jet break-up for encapsulation of cells, microbes and liquids in monodisperse microcapsules. Landbauforsch Volkenrode 2002;241:19.

[33] Wang L, Meng D. Fatty acid eutectic/polymethyl methacrylate composite as form-stable phase change material for thermal energy storage. Appl Energy 2010;87:2660–5.
[34] Wang W, Yang X, Fang Y, Ding J. Preparation and performance of form-stable polyethylene glycol/silicon dioxide composites as solid–liquid phase change materials. Appl Energy 2009;86:170–4.
[35] Li J, Xue P, He H, Ding W, Han J. Preparation and application effects of a novel form-stable phase change material as the thermal storage layer of an electric floor heating system. Energy Build 2009;41:871–80.
[36] Gravalos Moreno J, Calvo Herrera I., Mieres Royo J, Cubillo Capuz J, Simon B, María A., et al. Procedure for microencapsulation of phase change materials by spray-drying. EP Patent 2,119,498; 2009.
[37] Borreguero AM, Valverde JL, Rodríguez JF, Barber AH, Cubillo JJ, Carmona M. Synthesis and characterization of microcapsules containing Rubitherm®RT27 obtained by spray drying. Chem Eng J 2011;166:384–90.
[38] Hawlader MNA, Uddin MS, Khin MM. Microencapsulated PCM thermal-energy storage system. Appl Energy 2003;74:195–202.
[39] Fei B, Lu H, Qi K, Shi H, Liu T, Li X, et al. Multi-functional microcapsules produced by aerosol reaction. J Aerosol Sci 2008;39:1089–98.
[40] Li M, Rouaud O, Poncelet D. Microencapsulation by solvent evaporation: state of the art for process engineering approaches. Int J Pharm 2008;363:26–39.
[41] Özonur Y, Mazman M, Paksoy HÖ, Evliya H. Microencapsulation of coco fatty acid mixture for thermal energy storage with phase change material. Int J Energy Res 2006;30:741–9.
[42] Hawlader MNA, Uddin MS, Zhu HJ. Preparation and evaluation of a novel solar storage material: Microencapsulated paraffin. Int J Sol Energy 2000:20.
[43] Hawlader MNA, Uddin MS, Zhu HJ. Encapsulated phase change materials for thermal energy storage: Experiments and simulation. Int J Energy Res 2002;26:159–71.
[44] Bayés-García L, Ventolà L, Cordobilla R, Benages R, Calvet T, Cuevas-Diarte MA. Phase change materials (PCM) microcapsules with different shell compositions: preparation, characterization and thermal stability. Sol Energy Mater Sol Cells 2010;94:1235–40.
[45] Konuklu Y, Unal M, Paksoy HO. Microencapsulation of caprylic acid with different wall materials as phase change material for thermal energy storage. Sol Energy Mater Sol Cells B 2014;120:536–42.
[46] Butstraen C, Salaün F. Preparation of microcapsules by complex coacervation of gum Arabic and chitosan. Carbohydr Polym 2014;99:608–16.
[47] Shin Y, Yoo D-I, Son K. Development of thermoregulating textile materials with microencapsulated phase change materials (PCM). II. Preparation and application of PCM microcapsules. J Appl Polym Sci 2005;96:2005–10.
[48] Onder E, Sarier N, Cimen E. Encapsulation of phase change materials by complex coacervation to improve thermal performances of woven fabrics. Thermochim Acta 2008;467:63–72.
[49] Deveci S, Basal G. Preparation of PCM microcapsules by complex coacervation of silk fibroin and chitosan. Colloid Polym Sci 2009;287:1455–67.
[50] Zhang Y, Lin WJ, Yang R, Zhang YP, Zhang QW. Preparation and thermal property of phase change material microcapsules by phase separation. Trans Tech Publ 2007:2293–6.
[51] Yang R, Zhang Y, Wang X, Zhang Y, Zhang Q. Preparation of n-tetradecane-containing microcapsules with different shell materials by phase separation method. Sol Energy Mater Sol Cells 2009;93:1817–22.
[52] Wang L-Y, Tsai P-S, Yang Y-M. Preparation of silica microspheres encapsulating phase-change material by sol-gel method in O/W emulsion. J Microencapsul 2006;23:3–14.
[53] Zhang H, Wang X, Wu D. Silica encapsulation of n-octadecane via sol-gel process: a novel microencapsulated phase-change material with enhanced thermal conductivity and performance. J Colloid Interf Sci 2010;343:246–55.
[54] Chen Z, Cao L, Shan F, Fang G. Preparation and characteristics of microencapsulated stearic acid as composite thermal energy storage material in buildings. Energy Build 2013;62:469–74.
[55] Chen Z, Cao L, Fang G, Shan F. Synthesis and characterization of microencapsulated paraffin microcapsules as shape-stabilized thermal energy storage materials. Nanoscale Microscale Thermophys Eng 2013;17:112–23.
[56] Yu S, Wang X, Wu D. Microencapsulation of n-octadecane phase change material with calcium carbonate shell for enhancement of thermal conductivity and serving durability: synthesis, microstructure, and performance evaluation. Appl Energy 2014;114:632–43.
[57] Platte D, Helbig U, Houbertz R, Sextl G. Microencapsulation of alkaline salt hydrate melts for phase change applications by surface thiol-michael addition polymerization. Macromol Mater Eng 2013;298:67–77.
[58] Yadav SK, Suresh AK, Khilar KC. Microencapsulation in polyurea shell by interfacial polycondensation. AIChE J 1990;36:431–8.
[59] Yadav SK, Khilar KC, Suresh AK. Release rates from semi-crystalline polymer microcapsules formed by interfacial polycondensation. J Membr Sci 1997;125:213–8.
[60] Hong K, Park S. Preparation of polyurethane microcapsules with different soft segments and their characteristics. React Funct Polym 1999;42:193–200.
[61] Hong K, Park S. Preparation of polyurea microcapsules containing ovalbumin. Mater Chem Phys 2000;64:20–4.
[62] Cho J-S, Kwon A, Cho C-G. Microencapsulation of octadecane as a phase-change material by interfacial polymerization in an emulsion system. Colloid Polym Sci 2002;280:260–6.
[63] Kim J, Cho G. Thermal storage/release, durability, and temperature sensing properties of thermostatic fabrics treated with octadecane-containing microcapsules. Text Res J 2002;72:1093–8.
[64] Siddhan P, Jassal M, Agrawal AK. Core content and stability of n-octadecane-containing polyurea microencapsules produced by interfacial polymerization. J Appl Polym Sci 2007;106:786–92.
[65] Zhang H, Wang X. Synthesis and properties of microencapsulated n-octadecane with polyurea shells containing different soft segments for heat energy storage and thermal regulation. Sol Energy Mater Sol Cells 2009;93:1366–76.
[66] Su J-F, Wang L-X, Ren L. Synthesis of polyurethane microPCMs containing n-octadecane by interfacial polycondensation: influence of styrene-maleic anhydride as a surfactant. Colloids Surf A: Physicochem Eng Asp 2007;299: 268–275.
[67] Su J-F, Wang L-X, Ren L, Huang Z, Meng X-W. Preparation and characterization of polyurethane microcapsules containing n-octadecane with styrene-maleic anhydride as a surfactant by interfacial polycondensation. J Appl Polym Sci 2006;102:4996–5006.
[68] Guang-Long Z, Xiao-Zheng L, Zhi-Cheng T, Li-Xian S, Tao Z. Microencapsulation of n-hexadecane as a phase change material in polyurea. Acta Phys Chim Sin 2004;20:90–3.
[69] Lan X-Z, Tan Z-C, Zou G-L, Sun L-X, Zhang T. Microencapsulation of n-eicosane as energy storage material. Chin J Chem 2004;22:411–4.
[70] Liang C, Lingling X, Hongbo S, Zhibin Z. Microencapsulation of butyl stearate as a phase change material by interfacial polycondensation in a polyurea system. Energy Convers Manag 2009;50:723–9.
[71] Lone S, Lee HM, Kim GM, Koh W-G, Cheong IW. Facile and highly efficient microencapsulation of a phase change material using tubular microfluidics. Colloids Surf A: Physicochem Eng Asp 2013;422:61–7.
[72] Park S-J, Shin Y-S, Lee J-R. Preparation and characterization of microcapsules containing lemon oil. J Colloid Interf Sci 2001;241:502–8.
[73] Tseng Y-H, Fang M-H, Tsai P-S, Yang Y-M. Preparation of microencapsulated phase-change materials (MCPCMs) by means of interfacial polycondensation. J Microencapsul 2005;22:37–46.
[74] Gao GB, Qian CX, Gao MJ. Preparation and characterization of hexadecane microcapsule with polyurea-melamine formaldehyde resin shell materials. Chin Chem Lett 2010;21:533–7.
[75] Su J, Ren L, Wang L. Preparation and mechanical properties of thermal energy storage microcapsules. Colloid Polym Sci 2005;284:224–8.
[76] Khakzad F, Alinejad Z, Shirin-Abadi A, Ghasemi M, Mahdavian A. Optimization of parameters in preparation of PCM microcapsules based on melamine formaldehyde through dispersion polymerization. Colloid Polym Sci 2013:1–14.
[77] Wei J, Li Z, Liu L, Liu X. Preparation and characterization of novel polyamide paraffin MEPCM by interfacial polymerization technique. J Appl Polym Sci 2013;127:4588–93.
[78] Yuan HG, Kalfas G, Ray WH. Suspension polymerization. J Macromol Sci C 1991;31:215–99.
[79] Arshady R. Suspension, emulsion, and dispersion polymerization: a methodological survey. Colloid Polym Sci. 1992;270:717–32.
[80] Scully D. Scale-up in suspension polymerization. J Appl Polym Sci 1976;20:2299–303.
[81] Sánchez L, Sánchez P, de Lucas A, Carmona M, Rodríguez J. Microencapsulation of PCMs with a polystyrene shell. Colloid Polym Sci 2007;285:1377–85.
[82] Sánchez L, Sánchez P, Carmona M, de Lucas A, Rodríguez J. Influence of operation conditions on the microencapsulation of PCMs by means of suspension-like polymerization. Colloid Polym Sci 2008;286:1019–27.
[83] Sánchez L, Lacasa E, Carmona M, Rodríguez JF, Sánchez P. Applying an experimental design to improve the characteristics of microcapsules containing phase change materials for fabric uses. Ind Eng Chem Res 2008;47:9783–90.
[84] Sánchez-Silva L, Carmona M, de Lucas A, Sánchez P, Rodríguez JF. Scale-up of a suspension-like polymerization process for the microencapsulation of phase change materials. J Microencapsul 2010;27:583–93.
[85] Taguchi Y, Yokoyama H, Kado H, Tanaka M. Preparation of PCM microcapsules by using oil absorbable polymer particles. Colloids Surf A: Physicochem Eng Asp 2007;301:41–7.
[86] Sánchez-Silva L, Rodríguez JF, Romero A, Borreguero AM, Carmona M, Sánchez P. Microencapsulation of PCMs with a styrene-methyl methacrylate copolymer shell by suspension-like polymerisation. Chem Eng J 2010;157:216–22.
[87] Chang CC, Tsai YL, Chiu JJ, Chen H. Preparation of phase change materials microcapsules by using PMMA network-silica hybrid shell via sol-gel process. J Appl Polym Sci. 2009;112:1850-1857.
[88] You M, Zhang X, Wang J, Wang X. Polyurethane foam containing microencapsulated phase-change materials with styrene–divinybenzene co-polymer shells. J Mater Sci 2009;44:3141–7.
[89] You M, Wang X, Zhang X, Zhang L, Wang J. Microencapsulated n-octadecane with styrene–divinybenzene co-polymer shells. J Polym Res 2011;18:49–58.
[90] Borreguero AM, Carmona M, Sanchez ML, Valverde JL, Rodriguez JF. Improvement of the thermal behaviour of gypsum blocks by the incorporation of microcapsules containing PCMS obtained by suspension polymerization with an optimal core/coating mass ratio. Appl Therm Eng 2010;30:1164–9.
[91] Li W, Song G, Tang G, Chu X, Ma S, Liu C. Morphology, structure and thermal stability of microencapsulated phase change material with copolymer shell. Energy 2011;36:785–91.
[92] Wang H, Wang JP, Wang X, Li W, Zhang X. Preparation and properties of microencapsulated phase change materials containing two-phase core materials. Ind Eng Chem Res 2013;52:14706–12.

[93] Yin D, Ma L, Liu J, Zhang Q. Pickering emulsion: a novel template for microencapsulated phase change materials with polymer–silica hybrid shell. Energy. 2013.
[94] Huang J, Wang T, Zhu P, Xiao J. Preparation, characterization, and thermal properties of the microencapsulation of a hydrated salt as phase change energy storage materials. Thermochim Acta 2013;557:1–6.
[95] Wang T, Huang J, Zhu P, Xiao J. Fabrication and characterization of microencapsulated sodium phosphate dodecahydrate with different crosslinked polymer shells. Colloid Polym Sci 2013;291:2463–8.
[96] Baek KH, Lee JY, Kim JH. Core/shell structured PCM nanocapsules obtained by resin fortified emulsion process. J Dispers Sci Technol 2007;28:1059–65.
[97] Alkan C, SarI A, Karaipekli A, Uzun O. Preparation, characterization, and thermal properties of microencapsulated phase change material for thermal energy storage. Sol Energy Mater Sol Cells 2009;93:143–7.
[98] SarI A, Alkan C, Karaipekli A, Uzun O. Microencapsulated n-octacosane as phase change material for thermal energy storage. Sol Energy 2009;83: 1757–1763.
[99] Alay S, Göde F, Alkan C. Preparation and characterization of poly(methylmethacrylate-coglycidyl methacrylate)/n-hexadecane nanocapsules as a fiber additive for thermal energy storage. Fibers Polym 2010;11:1089–93.
[100] Alay S, Alkan C, Göde F. Synthesis and characterization of poly(methyl methacrylate)/n-hexadecane microcapsules using different cross-linkers and their application to some fabrics. Thermochim Acta 2011;518:1–8.
[101] SarI A, Alkan C, Karaipekli A. Preparation, characterization and thermal properties of PMMA/n-heptadecane microcapsules as novel solid-liquid microPCM for thermal energy storage. Appl Energy 2010;87:1529–34.
[102] Wang Y, Zhang Y, Xia T, Zhao W, Yang W. Effects of fabricated technology on particle size distribution and thermal properties of stearic–eicosanoic acid/polymethylmethacrylate nanocapsules. Sol Energy Mater Sol Cells Part B 2014;120:481–90.
[103] Ma S, Song G, Li W, Fan P, Tang G. UV irradiation-initiated MMA polymerization to prepare microcapsules containing phase change paraffin. Sol Energy Mater Sol Cells 20101643–7.
[104] Alay S, Göde F, Alkan C. Synthesis and thermal properties of poly(n-butyl acrylate)/n-hexadecane microcapsules using different cross-linkers and their application to textile fabrics. J Appl Polym Sci 2011;120:2821–9.
[105] Sukhorukov G, Fery A, Möhwald H. Intelligent micro- and nanocapsules. Prog Polym Sci 2005;30:885–97.
[106] Fang Y, Yu H, Wan W, Gao X, Zhang Z. Preparation and thermal performance of polystyrene/n-tetradecane composite nanoencapsulated cold energy storage phase change materials. Energy Convers Manag 2013;76:430–6.
[107] Tahan Latibari S, Mehrali M, Mehrali M, Indra Mahlia TM, Cornelis Metselaar HS. Synthesis, characterization and thermal properties of nanoencapsulated phase change materials via sol–gel method. Energy 2013;61:664–72.
[108] Fang Y, Kuang S, Gao X, Zhang Z. Preparation and characterization of novel nanoencapsulated phase change materials. Energy Convers Manag 2008;49: 3704–3707.
[109] Chen Z-H, Yu F, Zeng X-R, Zhang Z-G. Preparation, characterization and thermal properties of nanocapsules containing phase change material n-dodecanol by miniemulsion polymerization with polymerizable emulsifier. Appl Energy 2012;91:7–12.
[110] de Cortazar MG, Rodríguez R. Thermal storage nanocapsules by miniemulsion polymerization. J Appl Polym Sci 2013;127:5059–64.
[111] Fuensanta M, Paiphansiri U, Romero-Sánchez MD, Guillem C, López-Buendía ÁM, Landfester K. Thermal properties of a novel nanoencapsulated phase change material for thermal energy storage. Thermochim Acta 2013;565:95–101.
[112] Fang G, Li H, Yang F, Liu X, Wu S. Preparation and characterization of nanoencapsulated n-tetradecane as phase change material for thermal energy storage. Chem Eng J 2009;153:217–21.
[113] Hu X, Huang Z, Yu X, Li B. Preparation and thermal energy storage of carboxymethyl cellulose-modified nanocapsules. Bioenergy Res 2013;6:1135–41.
[114] Karthikeyan M., Ramachandran T., Sundaram O.S. Nanoencapsulated phase change materials based on polyethylene glycol for creating thermoregulating cotton. J Ind Text. 2013.
[115] Ghosh SK. Functional coatings: by polymer microencapsulation. Wiley-vch; 2006.
[116] Dorati R, Genta I, Modena T, Conti B. Microencapsulation of a hydrophilic model molecule through vibration nozzle and emulsion phase inversion technologies. J Microencapsul 2013;30:559–70.